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colorless crystal contains two discrete molecules in each unit cell. The compound crystallizes in the triclinic space group $\overline{P}1$, with unit cell dimensions of a 9.564(8), b 12.208(5), c 12.946(9) Å, α 100.00(5), β 100.41(8), γ 102.97(7) $^\circ$ and D_{calcd} 1.10 g cm $^{-3}$. The adduct has a relatively long Ga-P distance of 2.683(5) Å and the α -carbon atoms of the substituents on gallium and phosphorus are essentially but not perfectly eclipsed. The syntheses of $(\text{Me}_3\text{CCH}_2)_3\text{In}\cdot\text{P}(\text{H})\text{Ph}_2$ and $(\text{Me}_3\text{SiCH}_2)_3\text{In}\cdot\text{P}(\text{H})\text{Ph}_2$ were attempted but room temperature elimination reactions, which produced CMe_4 and SiMe_4 , respectively, and the appropriate organoindium phosphides, precluded the isolation of adducts. Simple kinetic studies revealed that $\text{In}(\text{CH}_2\text{CMe}_3)_3\cdot\text{P}(\text{H})\text{Ph}_2$ eliminated CMe_4 at 17°C significantly faster than $\text{In}(\text{CH}_2\text{SiMe}_3)_3\cdot\text{P}(\text{H})\text{Ph}_2$ produced SiMe_4 .

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The Chemistry of Diphenylphosphine Adducts of Tris(Neopentyl)-
and Tris(Trimethylsilylmethyl)-Gallium and -Indium Including the
Crystal and Molecular Structure of $(Me_3CCH_2)_3Ga \cdot P(H)Ph_2$

by

Michael A. Banks, O. T. Beachley, Jr., John D. Maloney
and Robin D. Rogers

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THE CHEMISTRY OF DIPHENYLPHOSPHINE ADDUCTS OF TRIS(NEOPENTYL)-
AND TRIS(TRIMETHYLSILYL)METHYL-GALLIUM AND -INDIUM INCLUDING THE
CRYSTAL AND MOLECULAR STRUCTURE OF $(Me_3CCH_2)_3Ga \cdot P(H)Ph_2$.

by

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Abstract

The adducts $(Me_3CCH_2)_3Ga \cdot P(H)Ph_2$ and $(Me_3SiCH_2)_3Ga \cdot P(H)Ph_2$ have been prepared as crystalline solids at room temperature and characterized by cryoscopic molecular weight measurements in benzene solution and 1H NMR, ^{31}P NMR and IR spectroscopic data. The molecular weight studies demonstrate that both adducts are extensively dissociated in solution and that $Ga(CH_2CMe_3)_3$ is a stronger Lewis acid than $Ga(CH_2SiMe_3)_3$. An X-ray structural study defined the nature of $(Me_3CCH_2)_3Ga \cdot P(H)Ph_2$ in the solid state. The colorless crystal contains two discrete molecules in each unit cell. The compound crystallizes in the triclinic space group $\bar{P}\bar{1}$ with unit cell dimensions of a 9.564(8), b 12.208(5), c 12.946(9) \AA , α 100.00(5), β 100.41(8), γ 102.97(7) $^\circ$ and D_{calcd} 1.10 g cm^{-3} . The adduct has a relatively long Ga-P distance of 2.683(5) \AA and the α -carbon atoms of the substituents on gallium and phosphorus are essentially but not perfectly eclipsed. The

syntheses of $(\text{Me}_3\text{CCH}_2)_3\text{In}\cdot\text{P}(\text{H})\text{Ph}_2$ and $(\text{Me}_3\text{SiCH}_2)_3\text{In}\cdot\text{P}(\text{H})\text{Ph}_2$ were attempted but room temperature elimination reactions, which produced CMe_4 and SiMe_4 , respectively, and the appropriate organoindium phosphides, precluded the isolation of adducts. Simple kinetic studies revealed that $\text{In}(\text{CH}_2\text{CMe}_3)_3\text{-P}(\text{H})\text{Ph}_2$ eliminated CMe_4 at 17°C significantly faster than $\text{In}(\text{CH}_2\text{SiMe}_3)_3\text{-P}(\text{H})\text{Ph}_2$ produced SiMe_4 .

Introduction

The compound semiconductors GaAs and InP have spurred a renewed interest in the chemistry of gallium and indium. Much of the characteristic chemistry of these group 13 elements can be related to the ability of the metal atom to accept an electron pair. Thus, organo-gallium and -indium compounds react with Lewis bases to form adducts. If the Lewis base has an acidic proton, an elimination reaction can occur typically at elevated temperatures to produce compounds of the type, R_2MER_2 . Thus, it is logical that compounds of the type MR_3 ,¹ $R_3M \cdot ER_3$ ² and R_2MER_2 ³ have been used as precursors for making the compound semiconductors.

A review of the literature⁴ suggests that all of the physical measurements of thermodynamic parameters related to stabilities of adducts and of the structural studies of homoleptic organo-gallium and -indium compounds with phosphorus and arsenic bases have involved $GaMe_3$ or $InMe_3$. The enthalpies of dissociation of $Me_3Ga \cdot L$ and $Me_3In \cdot L$ ($L = PMe_3$ and $AsMe_3$) were measured by vapor pressure techniques.⁵ Even though 1H NMR studies⁶ have been used to relate the ΔH_{diss} of $Et_3Ga \cdot PMe_3$ to $Me_3Ga \cdot PMe_3$, no quantitative studies have verified the early predictions. It is regrettable but no quantitative studies permit comparisons of the effects of different organic substituents on the Lewis acidities of organo-gallium and -indium compounds to a common Lewis base. There is also a surprising lack of structural information on adducts of gallium or indium. Only the adducts $Me_3M \cdot P(Ph)_2C_2H_4(Ph_2)P \cdot MMe_3$ ($M = Ga, In$),^{7,8} $Me_2ClGa \cdot P(Ph)_2CH_2P(Ph)_2$ ⁹ and $Cl_3Ga \cdot PMe_3$ ¹⁰ have been the subject of X-ray structural studies, whereas $Me_3Ga \cdot NMe_3$ ¹¹ and $Me_3Ga \cdot PMe_3$ ¹¹ have been investigated by electron diffraction techniques.

In this paper, we report the synthesis and characterization of two gallium-phosphorus adducts, $(\text{Me}_3\text{CCH}_2)_3\text{Ga}\bullet\text{P}(\text{H})\text{Ph}_2$ and $(\text{Me}_3\text{SiCH}_2)_3\text{Ga}\bullet\text{P}(\text{H})\text{Ph}_2$ and the attempted synthesis of $(\text{Me}_3\text{CCH}_2)_3\text{In}\bullet\text{P}(\text{H})\text{Ph}_2$ and $(\text{Me}_3\text{SiCH}_2)_3\text{In}\bullet\text{P}(\text{H})\text{Ph}_2$. The indium containing adducts were not sufficiently stable at room temperature to permit characterization due to the occurrence of elimination reactions. It is noteworthy that the X-ray structural study of $(\text{Me}_3\text{CCH}_2)_3\text{Ga}\bullet\text{P}(\text{H})\text{Ph}_2$ provides the first structure of an adduct of a heavier group 13 element with a Lewis base which incorporates an acidic hydrogen. Cryoscopic molecular weight studies of $(\text{Me}_3\text{CCH}_2)_3\text{Ga}\bullet\text{P}(\text{H})\text{Ph}_2$ and $(\text{Me}_3\text{SiCH}_2)_3\text{Ga}\bullet\text{P}(\text{H})\text{Ph}_2$ permit calculations of the percent dissociation of the adducts and, in turn, of the equilibrium constants for dissociation of the adducts. Thus, the effects of the neopentyl and trimethylsilylmethyl substituents on the Lewis acidities of the organo-gallium compounds have been evaluated quantitatively.

Experimental Section

All compounds described in this investigation were extremely sensitive to oxygen and moisture and were manipulated in a standard vacuum line or in a purified argon atmosphere. The gallium and indium alkyls, $\text{Ga}(\text{CH}_2\text{CMe}_3)_3$,¹² $\text{Ga}(\text{CH}_2\text{SiMe}_3)_3$,¹³ $\text{In}(\text{CH}_2\text{CMe}_3)_3$,¹⁴ and $\text{In}(\text{CH}_2\text{SiMe}_3)_3$,¹⁵ were prepared and purified by literature methods. Diphenylphosphine was purchased from Strem Chemicals, Inc. and purified by vacuum distillation. Solvents were dried by conventional procedures. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Infrared spectra of Nujol mulls between CsI plates were recorded by means of a Perkin-Elmer 683 spectrometer. Absorption intensities are reported with the abbreviations vs (very strong), s (strong), m (medium), w (weak), and sh (shoulder). The ¹H NMR spectra were recorded at 90 or 300 MHz by using either a Varian EM-390 or a Varian Gemini-300 spectrometer, respectively. Proton chemical shifts are reported in δ units (ppm) and are referenced to SiMe_4 as δ 0.00 and benzene as δ 7.13. The ³¹P NMR spectra were recorded at 36.23 or 161.90 MHz by using either a JEOL FX-90Q or a Varian VXR-400 spectrometer, respectively. Phosphorus chemical shifts are reported relative to 85% H_3PO_4 as δ 0.00 ppm. Negative values are assigned for shifts upfield of H_3PO_4 . All samples for NMR spectra were contained in sealed NMR tubes. Melting points were observed in sealed capillaries. Molecular weights were measured cryoscopically in benzene by using an instrument similar to that described by Shriver and Drezdzon.¹⁶

Synthesis of Tris(neopentyl)gallium(III)diphenylphosphine Adduct, $(\text{Me}_3\text{CCH}_2)_3\text{Ga}\bullet\text{P}(\text{H})\text{Ph}_2$. A 100-mL Schlenk flask was charged with 0.377 g (1.33 mmol) of $\text{Ga}(\text{CH}_2\text{CMe}_3)_3$ in the glove box. A tared screw-cap vial was used to weigh 0.248 g (1.33 mmol) of HPPh_2 . Anhydrous pentane was used to assure

quantitative transfer of the HPPh_2 to the reaction flask. The tared screw-cap vial was rinsed five times with aliquots of pentane (4 mL each time). The flask was fitted with an adapter, cooled to -196 °C and evacuated on the vacuum line. The resulting mixture was stirred for 10 min at ambient temperature and the pentane was then removed by vacuum distillation to leave 0.591 g of a colorless crystalline solid (1.26 mmol, 94.7% yield based on $\text{Ga}(\text{CH}_2\text{CMe}_3)_3$) of $(\text{Me}_3\text{CCH}_2)_3\text{Ga}\bullet\text{P}(\text{H})\text{Ph}_2$. Crystals suitable for an X-ray crystallographic study of $(\text{Me}_3\text{CCH}_2)_3\text{Ga}\bullet\text{P}(\text{H})\text{Ph}_2$ were obtained by allowing a melted sample of the compound to slowly flow down the wall of a Pyrex tube. $(\text{Me}_3\text{CCH}_2)_3\text{Ga}\bullet\text{P}(\text{H})\text{Ph}_2$. mp 33.0-34.0 °C. ^1H NMR (C_6D_6 , δ): 0.0689 m: 1.04 (s, - CH_2 -), 1.10 (s, - CMe_3), 5.20 (d, $J_{\text{PH}} = 232$ Hz, H-P), 6.99-7.40 (m, Ph); 0.138 m: 1.06 (s, - CH_2 -), 1.12 (s, - CMe_3), 5.22 (d, $J_{\text{PH}} = 241$ Hz, H-P), 6.99-7.40 (m, Ph). ^{31}P NMR (C_6D_6 , δ): 0.0689 m: -37.8 (d, $J_{\text{PH}} = 232$ Hz); 0.138 m: -36.5 (d of pentets, $J_{\text{PH}} = 241$ Hz, $^3J_{\text{PCCH}} = 8$ Hz). Cryoscopic molecular weight, (calculated molality, observed molality, a or per cent dissociation, K) (See Results and Discussion): 0.05223, 0.0828, 58.5%, 0.0431; 0.04632, 0.0732, 58.1%, 0.0372; 0.04154, 0.0668, 60.8%, 0.0392; 0.03284, 0.0532, 62.0%, 0.0446. Anal. Calcd.: C, 69.08; H, 9.47. Found: C, 65.77, 66.76; H, 9.42, 9.13 (See Results and Discussion.). IR (Nujol mull, cm^{-1}): 3075 (w), 3058 (w), 2730 (vw), 2710 (vw), 2328 (vw), 2318 (vw), 2280 (vw), 1968 (vw), 1955 (vw), 1870 (vw), 1803 (vw), 1585 (vw), 1570 (vw), 1567 (vw), 1552 (vw), 1545 (vw), 1432 (s), 1358 (vs), 1325 (vw), 1295 (vw), 1268 (vw), 1222 (s), 1160 (vw), 1155 (vw), 1130 (w), 1102 (w), 1065 (w), 1032 (w), 1020 (w), 997 (w), 960 (w), 925 (vw), 915 (vw), 908 (vw), 885 (m), 840 (vw), 805 (w), 738 (s), 721 (vs), 689 (vs), 670 (w, sh), 612 (vw, sh), 599 (m), 500 (m), 458 (w, sh), 450 (w), 425 (w), 412 (w), 380 (w), 285 (w), 282 (w), 270 (w).

Synthesis of Tris[(trimethylsilyl)methyl]gallium(III)diphenylphosphine Adduct, $(\text{Me}_3\text{SiCH}_2)_3\text{Ga}\bullet\text{P}(\text{H})\text{Ph}_2$. A 100-mL round-bottom flask equipped with a 15 mm Solv-Seal joint was charged with 0.390 g (1.18 mmol) of $\text{Ga}(\text{CH}_2\text{SiMe}_3)_3$. A tared screw-cap vial was charged with 0.220 g (1.18 mmol) of HPPH_2 . The HPPH_2 was transferred quantitatively to the round-bottom flask by multiple washings with anhydrous pentane (20 mL). The flask was fitted with an adapter and evacuated. The reaction mixture was stirred 15 min and the pentane was removed by vacuum distillation. A colorless, crystalline solid (0.514 g, 0.992 mmol, 84.4% of $(\text{Me}_3\text{SiCH}_2)_3\text{Ga}\bullet\text{P}(\text{H})\text{Ph}_2$) was isolated.

$(\text{Me}_3\text{SiCH}_2)_3\text{Ga}\bullet\text{P}(\text{H})\text{Ph}_2$. mp 23.5-24.2 °C. ^1H NMR (C_6D_6 , δ): 0.0689 m: 0.05 (s, - CH_2 -), 0.12 (s, - CMe_3), 5.21 (d, $J_{\text{PH}} = 232$ Hz, H-P), 6.98-7.37 (m, Ph); 0.138 m: 0.03 (s, - CH_2 -), 0.13 (s, - CMe_3), 5.23 (d, $J_{\text{PH}} = 240$ Hz, H-P), 6.98-7.37 (m, Ph). ^{31}P NMR (C_6D_6 , δ) 0.0689 m: -38.4 (d, $J_{\text{PH}} = 232$ Hz); 0.138 m: -37.7 (d of pentets, $J_{\text{PH}} = 240$ Hz, $^3J_{\text{PCCH}} = 8$ Hz).

Cryoscopic molecular weight (calculated molality, observed molality, a or per cent dissociation, K) (See Results and Discussion): 0.0492, 0.0794, 61.5, 0.0482; 0.0376, 0.0629, 67.4, 0.0523; 0.0375, 0.0628, 67.5, 0.0525; 0.0314, 0.0541, 72.1, 0.0586; 0.0312, 0.0519, 65.4, 0.0408. IR (Nujol mull, cm^{-1}): 3076 (w), 3058 (w), 3020 (w), 3005 (w), 2948 (s), 2895 (m), 2860 (m), 2685 (vw), 2475 (vw, br), 2340 (vw), 2325 (vw), 2285 (vw), 1970 (vw), 1950 (vw), 1928 (vw), 1875 (vw, br), 1850 (vw, br), 1805 (vw), 1584 (vw), 1571 (w), 1468 (m), 1433 (m), 1390 (w), 1350 (w), 1325 (w), 1292 (w), 1251 (s), 1240 (vs), 1180 (w), 1155 (vw), 1102 (w), 1065 (w), 1024 (w), 990 (m, br), 955 (m, sh), 920 (w, sh), 885 (m), 848 (vs), 822 (vs), 749 (vs), 739 (s, sh), 720 (vs), 678 (s), 610 (m), 594 (w), 568 (w), 548 (w), 520 (m), 506 (m), 448 (w), 429 (w), 412 (vw), 286 (vw), 256 (vw), 238 (w), 223 (w).

Reaction of $\text{Ga}(\text{CH}_2\text{SiMe}_3)_3$ with HPPh_2 , an NMR Scale Reaction. An NMR tube was charged with an aliquot of a solution containing 0.105 g (0.318 mmol) of $\text{Ga}(\text{CH}_2\text{SiMe}_3)_3$ and 0.0593 g (0.318 mmol), of HPPh_2 in 5 mL of benzene. The NMR tube was flame-sealed with a torch then both ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded. ^1H NMR (0.07 m, C_6H_6 , δ): 0.08 (s, 6 H, $-\text{CH}_2-$), 0.15 (s, 27 H, $-\text{CMe}_3$), 4.93 (one line of the doublet for H-P). ^{31}P NMR (C_6H_6 , δ): -39.3 (d, $J_{\text{PH}} = 240$ Hz).

Attempted Synthesis of Trisneopentylindium(III)diphenylphosphine Adduct, $(\text{Me}_3\text{CCH}_2)_3\text{In}\bullet\text{P}(\text{H})\text{Ph}_2$. A 100-mL round-bottom flask was charged with 0.357 g (1.09 mmol) of $\text{In}(\text{CH}_2\text{CMe}_3)_3$, 0.203 g (1.09 mmol) of HPPh_2 and 10 mL of pentane. The flask was evacuated and the mixture was stirred 30 min at ambient temperature. Pentane was removed by vacuum distillation and 0.484 g of a colorless solid was isolated. The ^{31}P NMR spectra indicated that both the adduct $(\text{Me}_3\text{CCH}_2)_3\text{In}\bullet\text{P}(\text{H})\text{Ph}_2$ and compound $(\text{Me}_3\text{CCH}_2)_2\text{InPPh}_2^{17}$ were present. **Mixture of $(\text{Me}_3\text{CCH}_2)_3\text{In}\bullet\text{P}(\text{H})\text{Ph}_2$ and $(\text{Me}_3\text{CCH}_2)_2\text{InPPh}_2$.** mp partial melting at 48.2-48.8 °C, followed by melting with decomposition of solid particles at 150-155 °C. ^{31}P NMR (C_6H_6 , δ): -31.1 (s, 1.4, $(\text{Me}_3\text{CCH}_2)_2\text{InPPh}_2$), -40.0 (d of pentets, 2.6, $J_{\text{PH}} = 260$ Hz, $(\text{Me}_3\text{CCH}_2)_3\text{In}\bullet\text{P}(\text{H})\text{Ph}_2$), -50.6 (s, 1.0, $[(\text{Me}_3\text{CCH}_2)_2\text{InPPh}_2]_2$).

Rates of Elimination Studies for $(\text{Me}_3\text{CCH}_2)_3\text{In}\bullet\text{P}(\text{H})\text{Ph}_2$. Equimolar amounts of $\text{In}(\text{CH}_2\text{CMe}_3)_3$ (0.346 g, 1.05 mmol) and HPPh_2 (0.197 g, 1.05 mmol) were combined in 0.963 g benzene by using the procedure described for the preparation of $(\text{Me}_3\text{CCH}_2)_3\text{Ga}\bullet\text{P}(\text{H})\text{Ph}_2$. After the reagents were thoroughly mixed, an aliquot of the 1.09 m (0.96 M) solution was transferred to an NMR tube. The tube was flame-sealed and the ^{31}P NMR spectra were recorded. The intensities of the lines for $(\text{Me}_3\text{CCH}_2)_2\text{InPPh}_2^{17}$, $[(\text{Me}_3\text{CCH}_2)_2\text{InPPh}_2]_2^{17}$ and $(\text{Me}_3\text{CCH}_2)_3\text{In}\bullet\text{P}(\text{H})\text{Ph}_2$ and/or free HPPh_2 were used to calculate the extent of

reaction at a variety of times after mixing. Time, extent of reaction (17°C): 19 h, 35 min, 0.221; 41 h, 0.325; 65 h, 0.436; 90 h, 15 min, 0.543; 115 h, 0.831; 138 h, 0.948; 161 h, 30 min, 0.971; 185 h, 30 min, 0.988.

Rate of Elimination Studies for $(\text{Me}_3\text{SiCH}_2)_3\text{In}\cdot\text{P}(\text{H})\text{Ph}_2$. A benzene solution of $\text{In}(\text{CH}_2\text{SiMe}_3)_3$ (0.397 g, 1.06 mmol, 1.09 m, 0.96 M) and HPPh_2 (0.197 g, 1.06 mmol, 1.09 m, 0.96 M) was prepared as described previously. The intensities of the lines for $(\text{Me}_3\text{SiCH}_2)_2\text{InPPh}_2$,¹⁷ $[(\text{Me}_3\text{SiCH}_2)_2\text{InPPh}_2]^{17}$ and $(\text{Me}_3\text{SiCH}_2)_3\text{In}\cdot\text{P}(\text{H})\text{Ph}_2$ and/or HPPh_2 were used to calculate the extent of reaction. Time, extent of reaction (17°C): 19 h, 35 min, 0.0942; 45 h, 20 min, 0.257; 67 h, 45 min, 0.269; 91 h, 25 min, 0.325; 185 h, 30 min, 0.501; 209 h, 35 min, 0.537.

X-ray Data Collection, Structure Determination, and Refinement for $(\text{Me}_3\text{CCH}_2)_3\text{Ga}\cdot\text{P}(\text{H})\text{Ph}_2$. A transparent single crystal of $(\text{Me}_3\text{CCH}_2)_3\text{Ga}\cdot\text{P}(\text{H})\text{Ph}_2$ was mounted in a thin-walled glass capillary under Ar and transferred to the goniometer. The space group was determined to be either the centric $\bar{P}1$ or acentric $P1$. Statistical tests indicated that the space group was centric and the subsequent solution and successful refinement of the structure in the space group $\bar{P}1$ confirmed this. A summary of data collection parameters is given in Table 1.

The geometrically constrained hydrogen atoms were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5 Å². Due to the relatively high thermal motion, the methyl and phosphorus hydrogen atoms were not included in the final refinement. Refinement of the nonhydrogen atoms with anisotropic temperature factors led to final values of $R = 0.102$ and $R_w = 0.114$. The low melting point is consistent with the observed high thermal motion in the 20 °C data collected. Resolvable static disorder was not evident.

Results and Discussion

Tris(neopentyl)gallium(III) reacts with diphenylphosphine to form the adduct, $(\text{Me}_3\text{CCH}_2)_3\text{Ga}\bullet\text{P}(\text{H})\text{Ph}_2$, a colorless, crystalline compound with a relatively low melting point of 33.0-34.0 °C. The structure of this compound as determined by an X-ray structural study and the labeling of the atoms is presented in Figures 1 and 2. Bond distances and bond angles are collected in Tables 2, 3 and 4. The low melting point of this compound was manifested in high thermal motion and relatively poor crystal quality. No resolvable disorder was observed and the rather large thermal parameters resulted in high standard deviations in bond lengths. Even so, this structure is significant because it is the first of an adduct of a heavier group 13 element compound with a group 15 Lewis base having an acidic proton.

The most striking structural feature of $(\text{Me}_3\text{CCH}_2)_3\text{Ga}\bullet\text{P}(\text{H})\text{Ph}_2$ is the extremely long Ga-P distance of 2.683(5) Å. Other addition compounds exhibit shorter gallium-phosphorus distances of 2.353(2) Å for $\text{Cl}_3\text{Ga}\bullet\text{PMe}_3$,¹⁰ 2.52(2) Å for $\text{Me}_3\text{Ga}\bullet\text{PMe}_3$ ¹¹ (electron diffraction studies), 2.535(2) Å for $\text{Me}_2\text{ClGa}\bullet\text{P}(\text{Ph})_2\text{CH}_2\text{P}(\text{Ph})_2$ ⁹ and 2.563(3) Å⁷ or 2.54(4) Å⁸ for $\text{Me}_3\text{Ga}\bullet\text{P}(\text{Ph})_2\text{C}_2\text{H}_4(\text{Ph})_2\text{P}\bullet\text{GaMe}_3$ (two structural studies of the same compound). The long gallium-phosphorus distance suggests that $(\text{Me}_3\text{CCH}_2)_3\text{Ga}\bullet\text{P}(\text{H})\text{Ph}_2$ is a relatively weak adduct.

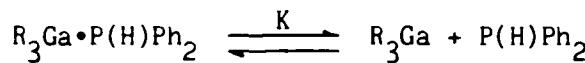
The second feature of interest in this structure relates to the observation that the α-carbon atoms of the substituents on gallium and phosphorus are essentially but not perfectly eclipsed. Thus, this observation suggests that the long gallium-phosphorus distance is probably not related to extreme steric stress. The other adduct with an eclipsed conformation $\text{Cl}_3\text{Ga}\bullet\text{PMe}_3$ ¹⁰ has the shortest of the known Ga-P bond distances.

In contrast, $\text{Me}_3\text{Ga}\bullet\text{P}(\text{Ph})_2\text{C}_2\text{H}_4(\text{Ph})_2\text{P}\bullet\text{GaMe}_3$ ^{8,9} is staggered. Both the gallium and phosphorus centers have rather distorted tetrahedral coordination environments. The C-Ga-C angles (117.0(7)-119.8(7)°) are typically greater than the normal tetrahedral values but not much smaller than the angle predicted for the uncoordinated trigonal planar monomeric Lewis acid. The C-P-C bond angle (103.4 (7)°) is less than the typical tetrahedral angle. In turn, the average P-Ga-C angle of 98(1)° is less than tetrahedral whereas the average Ga-P-C angle of 120(4)° is greater than tetrahedral. Although the hydrogen bonded to phosphorus was not located, the phosphorus atom is 0.48Å above the plane defined by Ga, C(16) and C(22). The two phenyl substituents are nearly perpendicular to each other, the dihedral angle between the planes defined by the aryl atoms is 85°. The neopentyl groups arrange themselves in propellar fashion around the Ga-P bond vector.

The elemental analyses of $(\text{Me}_3\text{CCH}_2)_3\text{Ga}\bullet\text{P}(\text{H})\text{Ph}_2$ for carbon and hydrogen were investigated but nonreproducible results were obtained. The observed percent carbon was low (69.08, calcd; 65.77, 66.76 found) whereas the observed percent hydrogen was within the range considered acceptable (9.47, calcd; 9.42, 9.13 found). These results suggest that the sample did not quantitatively decompose during analysis. Alternatively, the observation that the percent carbon is low might suggest that the sample was deficient in HPPh₂. Diphenylphosphine has a higher percent carbon (77.40) than $\text{Ga}(\text{CH}_2\text{CMe}_3)_3$ (63.61) or the adduct (69.08). A deficiency in HPPh₂ would be inconsistent with the observation that HPPh₂ is significantly less volatile than $\text{Ga}(\text{CH}_2\text{CMe}_3)_3$. If the sample was not $(\text{Me}_3\text{CCH}_2)_3\text{Ga}\bullet\text{P}(\text{H})\text{Ph}_2$ because one component was lost during isolation and purification, the more volatile component should have been lost and the experimental percent carbon should have been higher than that calculated for the adduct. The existence of a

crystalline solid at room temperature with a sharp melting point (33.0-34.0 °C) and the results of the X-ray structural study support the existence of a pure compound. Since nonreproducible analyses were obtained for $(\text{Me}_3\text{CCH}_2)_3\text{Ga}\bullet\text{P}(\text{H})\text{Ph}_2$, the related compound $(\text{Me}_3\text{SiCH}_2)_3\text{Ga}\bullet\text{P}(\text{H})\text{Ph}_2$ was not analyzed. It is noteworthy that other adducts of group 13 organometallic compounds have exhibited low elemental analyses for carbon.^{7,20}

Cryoscopic molecular weight studies of dilute benzene solutions of $(\text{Me}_3\text{CCH}_2)_3\text{Ga}\bullet\text{P}(\text{H})\text{Ph}_2$ and $(\text{Me}_3\text{SiCH}_2)_3\text{Ga}\bullet\text{P}(\text{H})\text{Ph}_2$ suggest that these adducts are significantly dissociated in solution. Tris(neopentyl)gallium-diphenylphosphine is less dissociated than the corresponding tris(trimethylsilylmethyl)gallium-diphenylphosphine adduct. The calculated (based on adduct) and the observed molalities of the solutions permit calculations of an apparent equilibrium constant for dissociation. Thus, $(\text{Me}_3\text{CCH}_2)_3\text{Ga}\bullet\text{P}(\text{H})\text{Ph}_2$ had an average constant of 0.0410 m (0.0360 M) whereas $(\text{Me}_3\text{SiCH}_2)_3\text{Ga}\bullet\text{P}(\text{H})\text{Ph}_2$



was 0.0505 m (0.0443 M). These results are consistent with the earlier suggestion^{12,14,21} that the neopentyl group has either stronger electron withdrawing or weaker electron donating properties but larger steric effects than the corresponding trimethylsilylmethyl substituent. Apparently, the electron withdrawing properties of the neopentyl group is the more important factor as $\text{Ga}(\text{CH}_2\text{CMe}_3)_3$ is observed to be the stronger Lewis acid.

The ^{31}P NMR spectra of solutions of $(\text{Me}_3\text{CCH}_2)_3\text{Ga}\bullet\text{P}(\text{H})\text{Ph}_2$ and $(\text{Me}_3\text{SiCH}_2)_3\text{Ga}\bullet\text{P}(\text{H})\text{Ph}_2$ support the hypothesis of equilibria between the adduct and the free acid and base as well as the conclusion that $\text{Ga}(\text{CH}_2\text{CMe}_3)_3$ is the stronger Lewis acid. As the concentrations of the

adduct systems increase, the chemical shifts of the ^{31}P NMR lines move to higher field and away from the chemical shift of the line for free $\text{P}(\text{H})\text{Ph}_2$. Similarly, $^1\text{J}_{\text{PH}}$ increases as the concentrations of the adduct systems increase. It is noteworthy that $\Delta\delta [\text{R}_3\text{Ga-P}(\text{H})\text{Ph}_2 - \text{P}(\text{H})\text{Ph}_2]$ is greater for $\text{R} = \text{CH}_2\text{CMe}_3$ (2.6 ppm), the stronger Lewis acid according to molecular weight studies, than for $\text{R} = \text{CH}_2\text{SiMe}_3$ (2.0 ppm). At the higher concentrations (0.138 m) $\Delta\delta$ increases to 3.9 ppm ($\text{R}=\text{CH}_2\text{CMe}_3$) and 2.7 ppm ($\text{R}=\text{CH}_2\text{SiMe}_3$). These studies clearly demonstrate that all investigations of Lewis acidities of group 13 compounds and/or Lewis basicities of phosphines by ^{31}P NMR spectroscopy must include concentration dependencies of spectra.

An attempt was also made to synthesize and fully characterize the neopentyl- and trimethylsilylmethyl-indium adducts of diphenylphosphine. However, the occurrence of elimination reactions at room temperature to form R_2InPPh_2 and RH precluded the isolation of pure adducts. The ^{31}P NMR spectra clearly revealed the presence of R_2InPPh_2 , $^{17}[\text{R}_2\text{InPPh}_2]_2^{17}$ and HPPh_2 , either free or as the adduct. The intensities of the lines related to the products of the elimination reaction, R_2InPPh_2 and $[\text{R}_2\text{InPPh}_2]_2$, increased with time whereas the line related to HPPh_2 decreased. When a solution at 17°C which was 1.09 m in both $\text{In}(\text{CH}_2\text{CMe}_3)_3$ and HPPh_2 was followed in a time dependent study, the elimination reaction was 54.3% complete after 90.2 h from the time of combining the reagents in benzene. In contrast, a 1.09 m solution of $\text{In}(\text{CH}_2\text{SiMe}_3)_3$ and HPPh_2 was 53.7% complete after 209.5 h. Thus, $\text{In}(\text{CH}_2\text{CMe}_3)_3\text{-P}(\text{H})\text{Ph}_2$ undergoes the elimination reaction at a significantly faster rate than does $\text{In}(\text{CH}_2\text{SiMe}_3)_3\text{-P}(\text{H})\text{Ph}_2$. If the rate law which is appropriate for the $\text{AlMe}_2\text{H-N(Me)(Ph)H}$ system²² is applicable to these organoindium-phosphine systems, then the rate constant for the elimination reaction and the equilibrium constant for

the formation of the adduct will influence the rate of reaction. If the equilibrium constants in the two indium-phosphorus systems are of similar magnitude to that observed for the related gallium-phosphorus systems, then the dominant factor to influence the rate of elimination will be the rate constant for reaction. The rate constant should be influenced by the charge on the α -carbon atom of the substituents bound to indium. The more strongly electron-withdrawing neopentyl substituted derivative would, in turn, be expected to have the faster rate of elimination, as observed. Kinetic studies for these indium-phosphorus systems will be the subject of a future publication.

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Table 1. Crystal Data and Summary of Intensity Data Collection and Structure Refinement.

Cmpd	$(Me_3CCH_2)_3Ga \cdot P(H)Ph_2$
Color/Shape	colorless/parallelepiped
For. wt.	469.34
Space group	P1
Temp., °C	20
Cell Constants ^a	
a, Å	9.564(8)
b, Å	12.208(5)
c, Å	12.946(9)
α, deg	100.00(5)
β, deg	100.41(8)
γ, deg	102.97(7)
Cell vol, Å ³	1412
Formula units/unit cell	2
D _{calc} , g cm ⁻³	1.10
μ _{calc} , cm ⁻¹	9.88
Diffractometer/Scan	Enraf-Nonius CAD-4/θ-2θ
Range of relative transm. factors, %	44/100
Radiation, graphite monochromator	MoKa ($\lambda=0.71073$)
Max crystal dimensions, mm	0.15x0.30x0.35
Scan width	0.80 + 0.35tanθ
Standard reflections	400; 050; 008
Decay of standards	±3.5%
Reflections measured	4369
2θ range, deg	2 ≤ 2θ ≤ 48
Range of h,k,l	+10, ±13, ±14
Reflections observed [$F_o \geq 5\sigma(F_o)$] ^b	2433
Computer programs ^c	SHELX ¹⁸
Structure solution	Heavy atom techniques
No. of parameters varied	262
Weights	unit
GOF	2.51
$R = \Sigma F_o - F_c / \Sigma F_o $	0.102
R _w	0.114
Largest feature final diff. map	1.0 Å ⁻³ near Ga

^aLeast-squares refinement of $((sin\theta)/\lambda)^2$ values for 20 reflections $\theta > 20^\circ$.^bCorrections: Lorentz-polarization and absorption (empirical, psi scan).^cNeutral scattering factors and anomalous dispersion corrections from ref 19.

Table 2. Interatomic Distances (\AA) for $(\text{Me}_3\text{CCH}_2)_3\text{Ga}\cdot\text{P}(\text{H})\text{Ph}_2$.

(A) Gallium-Phosphorus Distance

Ga-P 2.683(5)

(B) Gallium-Carbon Distances

Ga-C(1)	2.01(1)
Ga-C(6)	1.87(2)
Ga-C(11)	2.04(1)

(C) Phosphorus-Carbon Distances

P-C(16)	1.83(1)
P-C(22)	1.79(2)

(D) Neopentyl Carbon-Carbon Distances

C(1)-C(2)	1.52(2)	C(6)-C(7)	1.60(2)	C(11)-C(12)	1.45(2)
C(2)-C(3)	1.56(2)	C(7)-C(8)	1.50(2)	C(12)-C(13)	1.60(2)
C(2)-C(4)	1.51(2)	C(7)-C(9)	1.49(3)	C(12)-C(14)	1.51(2)
C(2)-C(5)	1.56(2)	C(7)-C(10)	1.58(3)	C(12)-C(15)	1.56(2)

(E) Phenyl Carbon-Carbon Distances

C(16)-C(17)	1.36(2)	C(22)-C(23)	1.36(2)
C(16)-C(21)	1.43(2)	C(22)-C(27)	1.43(2)
C(17)-C(18)	1.38(2)	C(23)-C(24)	1.37(2)
C(18)-C(19)	1.33(4)	C(24)-C(25)	1.40(2)
C(19)-C(20)	1.30(5)	C(25)-C(26)	1.34(2)
C(20)-C(21)	1.41(3)	C(26)-C(27)	1.37(2)

Table 3. Angles (in deg) for $(\text{Me}_3\text{CCH}_2)_3\text{Ga}\bullet\text{P}(\text{H})\text{Ph}_2$.

(A) Angles around the Gallium Atom

P-Ga-C(1)	98.0(5)	C(1)-Ga-C(6)	117.3(7)
P-Ga-C(6)	96.4(7)	C(1)-Ga-C(11)	117.0(7)
P-Ga-C(11)	100.0(7)	C(6)-Ga-C(11)	119.8(7)

(B) Angles around the Phosphorus Atom

Ga-P-C(16)	119.0(5)
Ga-P-C(22)	121.7(5)
C(16)-P-C(22)	103.4(7)

(C) Gallium-Carbon-Carbon Angles

Ga-C(1)-C(2)	124(1)
Ga-C(6)-C(7)	131(1)
Ga-C(11)-C(12)	125(1)

(D) Phosphorus-Carbon-Carbon Angles

P-C(16)-C(17)	122(1)	P-C(22)-C(23)	126(1)
P-C(16)-C(21)	118(1)	P-C(22)-C(27)	119(1)

(E) Neopentyl Carbon-Carbon-Carbon Angles

C(1)-C(2)-C(3)	110(1)	C(11)-C(12)-C(13)	108(1)
C(1)-C(2)-C(4)	111(1)	C(11)-C(12)-C(14)	115(2)
C(3)-C(2)-C(4)	110(2)	C(13)-C(12)-C(14)	110(1)
C(1)-C(2)-C(5)	108(1)	C(11)-C(12)-C(15)	109(2)
C(3)-C(2)-C(5)	110(1)	C(13)-C(12)-C(15)	106(1)
C(4)-C(2)-C(5)	109(2)	C(14)-C(12)-C(15)	108(2)
C(6)-C(7)-C(8)	115(1)		
C(6)-C(7)-C(9)	103(2)		
C(8)-C(7)-C(9)	110(2)		
C(6)-C(7)-C(10)	107(2)		
C(8)-C(7)-C(10)	108(2)		
C(9)-C(7)-C(10)	112(2)		

(F) Phenyl Carbon-Carbon-Carbon Angles

C(17)-C(16)-C(21)	120(2)	C(23)-C(22)-C(27)	115(1)
C(16)-C(17)-C(18)	122(2)	C(22)-C(23)-C(24)	124(1)
C(17)-C(18)-C(19)	119(3)	C(23)-C(24)-C(25)	120(2)
C(18)-C(19)-C(20)	120(3)	C(24)-C(25)-C(26)	116(2)
C(19)-C(20)-C(21)	127(3)	C(25)-C(26)-C(27)	125(2)
C(16)-C(21)-C(20)	113(2)	C(22)-C(27)-C(26)	120(2)

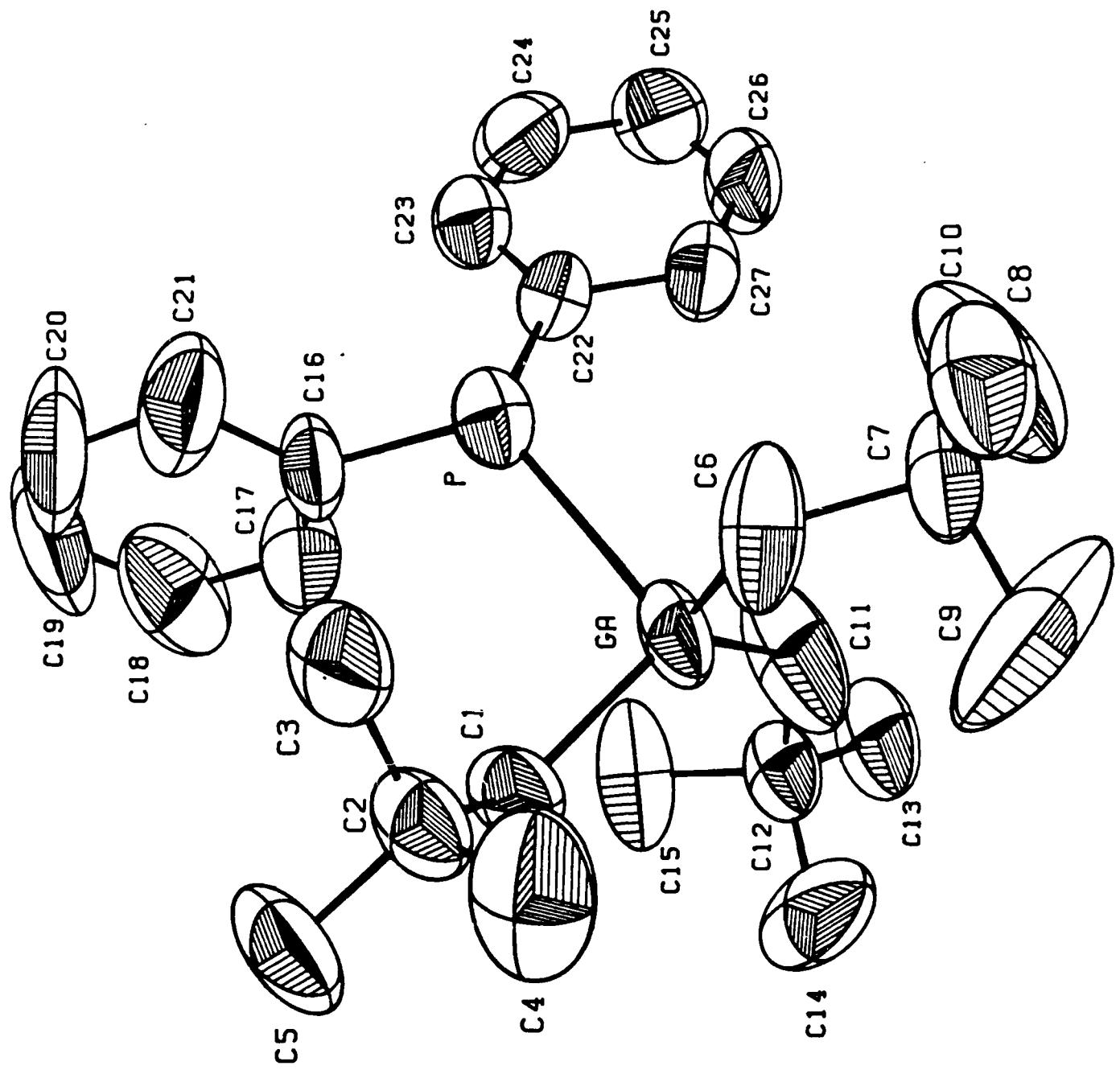
Table 4. Torsion Angles (in deg) for $(\text{Me}_3\text{CCH}_2)_3\text{Ga}\cdot\text{P}(\text{H})\text{Ph}_2$.

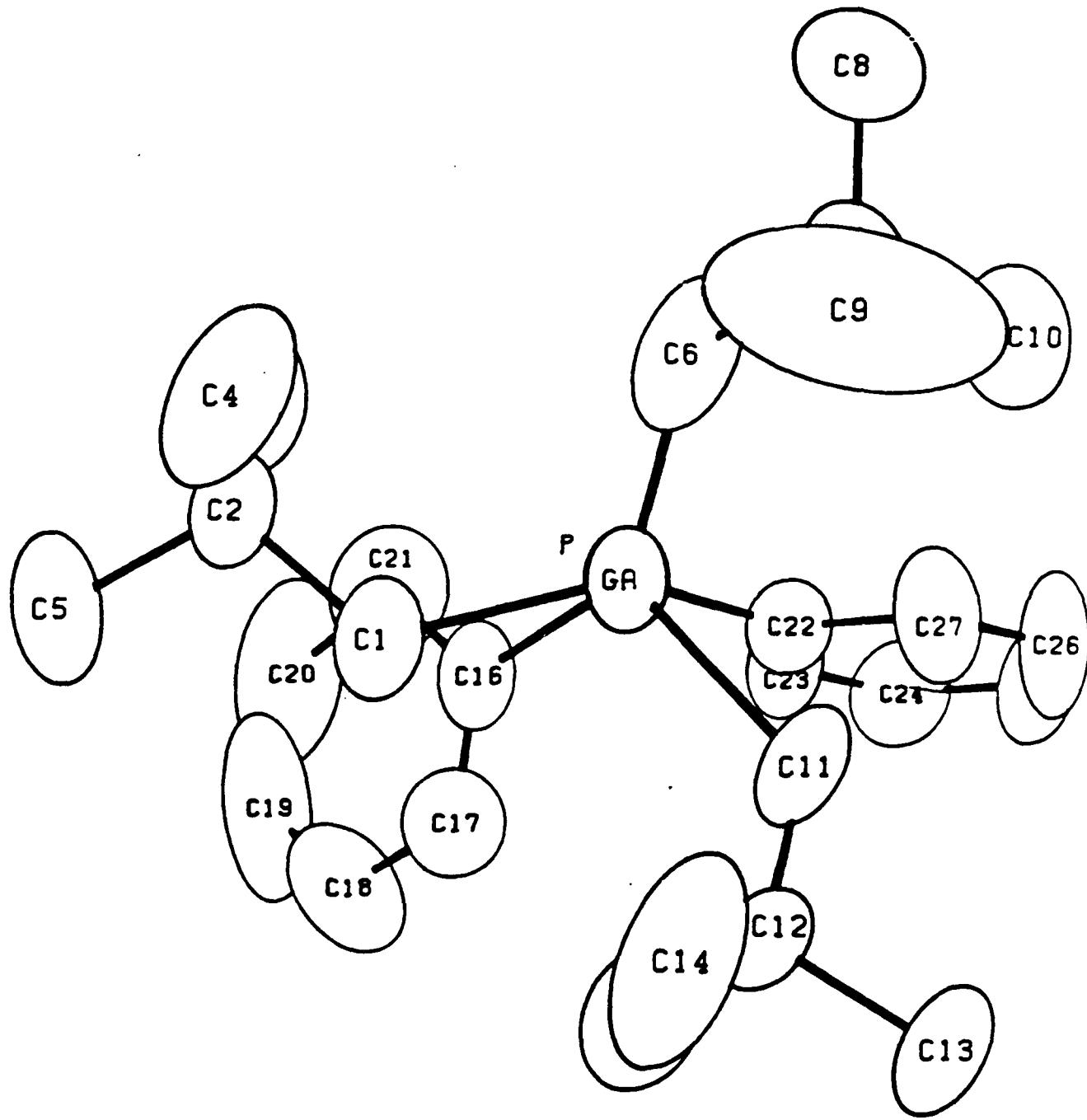
C(1)-Ga-P-C(16)	-19.2
C(1)-Ga-P-C(22)	-150.0
C(6)-Ga-P-C(16)	-138.0
C(6)-Ga-P-C(22)	91.2
C(11)-Ga-P-C(16)	100.1
C(11)-Ga-P-C(22)	-30.7

Captions for Figures

Figure 1. Labeling of atoms in $(\text{Me}_3\text{CCH}_2)_3\text{Ga}\cdot\text{P}(\text{H})\text{Ph}_2$. ORTEP diagram with thermal ellipsoids at the 50% probability level.

Figure 2. Projection of $(\text{Me}_3\text{CCH}_2)_3\text{Ga}\cdot\text{P}(\text{H})\text{Ph}_2$ down the Ga-P bond.





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